



Steam catalytic cracking of heavy naphtha (C₁₂) to high octane naphtha over B-MFI zeolite



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ABSTRACT

Continues consuming of fuel from fossil oil reservoirs due to the increase in energy demands encouraged scientists to use the pyrolysis of biomass in the production of clean energy. One of the most important product from the pyrolysis of biomass is dodecane. However, dodecane requires a further transformation in order to produce lighter hydrocarbons. Borosilicalite-1 (B-MFI) was synthesized with different mineralizer agents and utilized for steam catalytic cracking of dodecane. Furthermore, the amount of cooperative incorporation of boron to zeolitic framework contributes in adjusting the zeolitic acidity and consequently the amount of weak acid sites were observed to be proportional to the contents of boron. However, from pyridine-FTIR analysis, it was noticed that the acid site nature of borosilicalite-1 samples exhibited Brønsted acid site. Nevertheless, the presence of alkali fluoride as mineralizer agent enhanced the presence of boron in tetrahedral coordination system, which led to lower catalytic activity. While samples synthesized in the presence of alkali hydroxide were catalytically more active in steam catalytic cracking of dodecane due to its exhibit in trigonal coordination system. It was found that borosilicalite-1 was more stable when it was synthesized in the presence of sodium hydroxide as mineralizer agent rather than potassium hydroxide and the conversion was reached to 95% at 350 °C with space velocity of 4 h⁻¹ when the Si/B ratio was 10.

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1. Introduction

Large consumption of fossil oil reservoirs due to the increase in energy demands encouraged scientists to further explore renewable energy sources such as biomass. Many researchers conducted the use of energy crops as clean fuel due to the huge availability of biomass sources such as fast growing trees, switchgrass and agricultural residues. The scientific attention to the biomass has been increasing due to the wishes of global institutions and researchers in utilizing the environmental friendly clean energy. This is an important source, not only for the production of energy, but also for the drastic reduction in the volume of solid residue [1,2]. Furthermore, the political twists and turns toward the crude oil and price instability, encouraged numerous research organizations to have a closer look to biomass. Moreover, negligible emissions of toxic and

hazardous gases such as SO₂ and NO_x gasses served as the biggest cheerleader in the exploitation of biomass [1].

The technical intermediary for the conversion of biomass and the dismantling of these organic materials is the pyrolysis process. The pyrolysis of biomass can end up with valuable products such as syngas, solid bio-char and liquid bio-oil [1]. However, by further focusing on the bio-oil and the possible products from the pyrolysis of biomass, it was found that dodecane (C₁₂) is one of the most selected product from the pyrolysis process [1]. As the industrial importance of light hydrocarbons in many industrial field, it is important to study the transformation of non-usable chemical compounds to demanded chemical products such as light olefins, light paraffin and aromatics.

The catalytic conversion of dodecane can be carried out over heterogeneous catalysts. Due to the availability of different kinds of heterogeneous catalysts, it is worthy to note that most reactions in petrochemical industries occurs over zeolitic materials due to their adsorption properties for hydrocarbon molecules [3]. The nature of these zeolitic materials made them important to be used in multiple petrochemical processes such as alkylation, catalytic cracking,

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steam catalytic cracking and methanol-to-olefins [4–7]. However, the properties of these zeolitic materials should be compatible with the type of the process to notch up the desired goal such as high conversion, high selectivity and high stability. In order to recognize the role of these properties, that are offering the high selectivity, high conversion and long stability in zeolites, it is important that we identify the general factors that help these parameters to be improved.

By considering the nature of silicalite-1, for instance, it is inorganic microporous crystalline catalysts which is mainly consists of T atoms (where T is Si for silicalite-1) in tetrahedra coordination system (TO_4) [8,9]. By looking to the nature of physical properties, silicalite-1 has weak acid site due to the presence of silanol group and the absence of various elements such as aluminum, boron, gallium, et cetera. [10]. However, one of the most interested areas in the catalytic modifications is the isomorphous incorporation of tri- and/or tetravalent atoms to the zeolitic framework to modify the physical properties of the zeolites due to its influence in diversifying the catalytic properties of zeolites. Numerous researches studied the isomorphous incorporations of different kinds of heteroatoms such as aluminum [11–13] and boron [14–16] to solve classical problems such as low conversion and rapid deactivation.

Various zeolites with several topologies were used in steam catalytic cracking of dodecane [17,18]. Still, the issue of fast deactivation and low conversion in the catalytic cracking of dodecane need to be solved by modifying the physical properties of the zeolites. One of the most important zeolite is a 3-dimensional ZSM-5 (MFI) zeolite, which has excellent activity in many catalytic reactions [13,17,19]. Its wonderful activity has made it one of the most studied zeolite with different tri- and tetravalent atoms. However, the incorporation of boron in MFI topology is expected to add valuable feature due to the influence of boron on the strength of zeolitic acidity. As compared to aluminum, boron has weaker acid sites, which can be interesting for some catalytic cracking. This weaker acid sites are due to the high electronegativity feature of the boron, which make it difficult to chair the pair electrons. Borosilicalite-1 is well known for several kinds of reactions and it was firstly reported by Taramasso et al. [20]. However, further exploration is required for borosilicalite-1 to be used in the catalytic cracking of dodecane.

In this study, we synthesized boron containing MFI type zeolite (borosilicalite-1) under microwave irradiation. Furthermore, borosilicalite-1 was synthesized in the presence of different alkali hydroxide and alkali fluoride sources as mineralizer agent. The effect of isomorphous incorporation of boron in MFI type zeolite was systematically studied by X-ray analysis, N_2 physisorption measurements, NH_3 temperature program desorption, pyridine adsorption, NMR MAS spectra and it was evaluated in steam catalytic cracking of n-dodecane.

2. Experimental

2.1. Catalyst preparation

The synthesis of borosilicalite-1 (B-MFI) was achieved by the following chemicals without further purification: (1) colloidal silica (40 wt.% suspension in H_2O , LUDOX[®] HS-40, Sigma-Aldrich), (2) boric acid (ACS reagent, $\geq 99.5\%$, Sigma-Aldrich), (3) tetrapropyl-ammonium hydroxide solution (TPAOH, 1.0 M in H_2O , Sigma-Aldrich), (4) sodium hydroxide (NaOH, Panreac), (5) sodium fluoride (Sigma-Aldrich), (6) potassium fluoride (Sigma-Aldrich).

Borosilicalite-1 (B-MFI) zeolite was synthesized by further modification to our previous work [21]. Synthesis was performed by one of the following cases: (i) B-MFI was synthesized in the presence of different mineralizer agents; (ii) B-MFI was synthesized with different Si/B ratios in the presence of sodium hydroxide; (iv) B-MFI

Table 1

Molar ratio of the synthesized borosilicalite-1.

Molar ratio
1.0 SiO_2 : 0.1 TPAOH: 35.5 H_2O : (0–0.1) $\text{B}(\text{OH})_3$
1.0 SiO_2 : 0.1 TPAOH: 35.5 H_2O : (0–0.2) $\text{B}(\text{OH})_3$: 0.10 NaOH
1.0 SiO_2 : 0.1 TPAOH: 35.5 H_2O : 0.1 $\text{B}(\text{OH})_3$: 0.10 NaF
1.0 SiO_2 : 0.1 TPAOH: 35.5 H_2O : 0.1 $\text{B}(\text{OH})_3$: 0.10 KF
1.0 SiO_2 : 0.1 TPAOH: 35.5 H_2O : 0.1 $\text{B}(\text{OH})_3$: 0.10 KOH

was synthesized with different Si/B ratios in the absence of sodium hydroxide. Generally, B-MFI was synthesized with following procedure and steps: mineralizer agent (Xg) was dissolved in 38.85 g of deionized (DI) water, followed by adding 10.42 g of 1 M TPAOH and the solution was stirred for a few minutes. After that, colloidal silica (13.00 g) was added to the mixture. After the homogeneity of the mixture, boric acid (Yg) was added to the mixture. The reaction mixture was stirred slowly at ambient temperature for 2 h. The general gel composition was 1.0 SiO_2 : 0.1 TPAOH: 35.5 H_2O : (0–0.2) $\text{B}(\text{OH})_3$: (0–0.10) wF or wOH, where w is (Na or K). In one of the procedures to synthesize borosilicalite-1, X was 0.346 g of sodium hydroxide and Y was 0.54 g of boric acid. Experiments were carried out with different molar ratios as shown in Table 1.

The synthesized solution was transferred to 100 mL PTFE bottle and heated using microwave irradiation using the following program: (i) raising the temperature from room temperature to 180 °C in 5 min, (ii) dwelling the temperature at 180 °C for 2 h, (iii) cooling the system. During the synthesis time, the solution was stirred by 30% under microwave irradiation. The product was collected and washed thoroughly with DI water to reduce the pH. The samples were dried and then calcined at 550 °C for 5 h.

B-MFI zeolite was ion-exchanged with 2 M solution of ammonium nitrate under microwave irradiation at 85 °C for 10 min. For each 60 g of the solution, 3 g of the B-MFI zeolite was added and transferred to 100 mL Teflon bottle to carry out the ion-exchange process. After the first ion-exchange, samples were centrifuged once and the second ion-exchange was carried out again. After that, the samples washed twice with deionized water and re-calcined again at 550 °C for 5 h.

2.2. Catalyst characterization

2.2.1. Determination of crystallinity, phase purity, and morphology

X-ray diffraction (XRD, Rigaku Miniflex diffractometer) equipped with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) was used to identify the crystallinity and phase purity of B-MFI zeolite samples. XRD patterns were collected in the 2θ range of 5–50° with a step size of 0.02° and a scan speed of 3°/min. Field-emission scanning electron microscopy (FE-SEM, LYRA 3 Dual Beam, Tescan) was utilized to investigate the crystal morphologies and particle sizes of borosilicalite-1.

2.2.2. Determination of physicochemical properties, acidity and zeolitic structure

The textural properties of the parent sample and the modified B-MFI zeolites were evaluated using nitrogen adsorption–desorption isotherm. The Brunauer–Emmett–Teller (BET) surface area of the samples, external surface area and pore volume were evaluated.

The weak and strong acid sites were determined by temperature-programmed desorption of ammonia (NH_3 -TPD). The analysis was performed using a Chemisorb 2750 Micrometrics chemisorption analyzer. Zeolite sample (about 110 mg) was pre-treated at 600 °C for 1 h under the continuous flow of helium at 25 mL/min. Afterwards, sample allowed to cool to 100 °C followed by flowing NH_3 (10% NH_3 in helium) at flow rate of 25 mL/min

for 30 min to assure the saturation of the sample, followed by the removal of physisorbed NH_3 by purging the sample with helium for 1 h. The sample was heated to 650°C at constant rate of $10^\circ\text{C}/\text{min}$ to desorb the remaining NH_3 , and the TPD signal was monitored by a thermal conductivity detector (TCD) simultaneously.

Fourier transform infrared spectroscopy (FTIR, Nicolet NEXUS-FTIR-670 spectrometer) was used to collect FTIR spectra. Zeolite sample (0.22 wt%) was mixed with KBr and pressed into a wafer (50 mg). Subsequently, spectra were recorded. For OH stretching region, self-supported wafer (35 mg) was placed in a self-made cell and heated at 500°C for 1 h under vacuum. Subsequently, sample was cooled to 150°C and spectra were recorded between 4000 and 3200 cm^{-1} . After that, sample was exposed to pyridine vapor at 150°C for 30 min to determine Lewis and Brønsted acids. Afterwards, sample was evacuated to remove the physisorbed pyridine at 150°C for 1 h and the IR spectra was recorded.

The high-resolution ^{11}B and ^{29}Si MAS NMR spectra were obtained on a JEOL ECA-600 spectrometer (14.1 T) equipped with an additional 1 kW power amplifier. Solid-state ^{11}B and ^{29}Si MAS NMR spectra were used to identify the coordination of boron and silica. Solid-state ^{11}B MAS NMR spectra of borosilicalite-1 samples were carried out at a resonance frequency of 192.6 MHz, the pulse width was set at $3.4\text{ }\mu\text{s}$ and 10000 scans were accumulated at a sample spinning rate of 15 kHz with a 0.5 (s) relaxation delay. For ^{29}Si MAS NMR analysis was performed at a resonance frequency of 119.2 MHz, the pulse width was set at $4.1\text{ }\mu\text{s}$ and 10,000 scans were accumulated at a sample spinning rate of 15 kHz with a 30 (s) relaxation delay.

2.2.3. Determination of catalytic performance

The catalytic performance of borosilicalite-1 (B-MFI) samples was evaluated in the steam catalytic cracking (SCC) of dodecane process in a fixed bed reactor at atmospheric pressure. A catalyst volume of 1.5 cm^3 was used for all the catalyst testing procedures to evaluate the steam catalytic cracking at 350°C . Dodecane and water were fed to the fixed bed reactor with dodecane to steam ratio of 9:1 vol/vol using electric driven HPLC liquid injector pumps. The flow rates of dodecane and water were maintained at liquid space velocity (LHSV) of 4 h^{-1} . Nitrogen gas was employed as carrier gas, and its flow rate was maintained at 30 mL/min. Products were analyzed using an offline GC–MS (Agilent J&W DM5 ms GC column $50\text{ m} \times 0.20\text{ mm} \times 0.33\text{ }\mu\text{m}$).

3. Results and discussion

3.1. Effect of mineralizer agent source and boron content on crystallinity, phase purity, and morphology

The synthesis of silicalite-1 and its modification was studied in our previous work [21]. We reported that silicalite-1 can be synthesized in the presence of different mineralizer agents under microwave irradiation. However, in this work, further modifications on the synthesis formulation were performed to synthesize boron containing MFI type zeolite (borosilicalite-1). Three different strategies were used in the synthesis of borosilicalite-1 by adding boron as a heteroatom to the framework of MFI; (i) borosilicalite-1 was synthesized in the presence of different mineralizer agents, (ii) borosilicalite-1 was synthesized with different Si/B ratio in the absence of mineralizer agents, (iii) borosilicalite-1 was synthesized with different Si/B ratio in the presence of sodium hydroxide as mineralizer agent.

The effect of mineralizer agents was studied at constant Si/B ratio to estimate the role of the mineralizer agent source on the crystallinity, phase purity, morphology, textural properties, acidity, chemical structure and catalytic performance. Different

mineralizer agents were used, namely, sodium fluoride, potassium fluoride, sodium hydroxide and potassium hydroxide. However, these chemical sources have different physical and chemical properties. Sodium hydroxide and potassium hydroxide are categorized as strong base since they dissociate completely to Na^+ or K^+ and OH^- ions in water. While hypothetically, sodium fluoride and potassium fluoride are basic salt resulted from the reaction of strong base (NaOH or KOH) and weak acid (HF).

When these fluoride sources were added to water, they will dissolve in water followed by the hydrolysis of the weak ions (F^-) to HF in an equilibrium (reversible) reaction [22]. As a hypothesis, the effect of mineralizer agent on the framework structure was expected to be significant. However, it will be discovered through this manuscript.

XRD patterns of borosilicalite-1 samples which were synthesized with Si/B ratio of 10 in the presence of different mineralizer agents are shown in Fig. 1. The characteristic peaks of the produced B-MFI zeolite were successfully obtained and it was confirmed that all samples are well crystalline. It was observed that the intensity of these characteristic peaks were more pronounced when the sol-gel mixture was synthesized in the presence of alkaline source, which suggests that the alkaline source enhanced the crystal growth. On the second and third strategies, borosilicalite-1 was synthesized with different Si/B ratios in the absence or presence of sodium hydroxide as mineralizer agent. As shown in Fig. 2A, when the alkaline source was absent, the lowest Si/B ratio that was successfully obtained was 10. However, when sodium hydroxide was added, the crystallization was enhanced and it was possible to synthesize borosilicalite-1 with Si/B ratio of 5. Further decrease in Si/B ratio led to amorphous materials. This was attributed to the role of sodium hydroxide to enhance the crystallization rate. The availability of a limited organic structure directing agent in the framework allows boron to incorporate in a limited concentration. Further addition of organic structure directing agent or alkaline source are essential when low silicon to boron (or aluminium) ratio is targeted to neutralize the charge density in the framework, in which the later facilitate the incorporation and crystallization [23].

When the alkaline source was absent, the intensity of the characteristic peaks of MFI zeolite were more pronounced in the case of silicalite-1 as compared to borosilicalite-1 for same period of synthesis time and synthesis temperature as shown in Fig. 2A. This enhancement is due to the availability of less charge density in sol-gel mixture, which led to easier crystallization. While the addition of tri/tetravalent atoms such as boron contributed in disturbing the net charge density of the solution, which is the later decrease the crystallization rate. The decrease of crystallization rate is also observed to be proportional to the content of boron in the sol-gel mixture. On the other hand, when sodium hydroxide was added to the synthesis mixture, the intensity of the characteristic peaks was less pronounced in the absence of boron, as shown in Fig. 2B, due to the availability of additional charge density coming from the free sodium ions in the solution. However, the increase in the crystallization rate in borosilicalite-1 can be enhanced by adding a limited amount of counter ions such as sodium from sodium hydroxide to balance the charge density of the solution.

The morphology and particle size of the synthesized borosilicalite-1 were characterized using field emission scanning electron microscopy (FE-SEM). As shown in Fig. 1, when borosilicalite-1 was synthesized with different mineralizer agents, the morphology was with bolt and nut shape. However, the source of the mineralizer agent has no influence on the size and morphology of the borosilicalite-1. Nevertheless, when borosilicalite-1 was synthesized in the absence of mineralizer agents, the morphology was irregular and the particle size was varied as shown in Fig. 1(e).

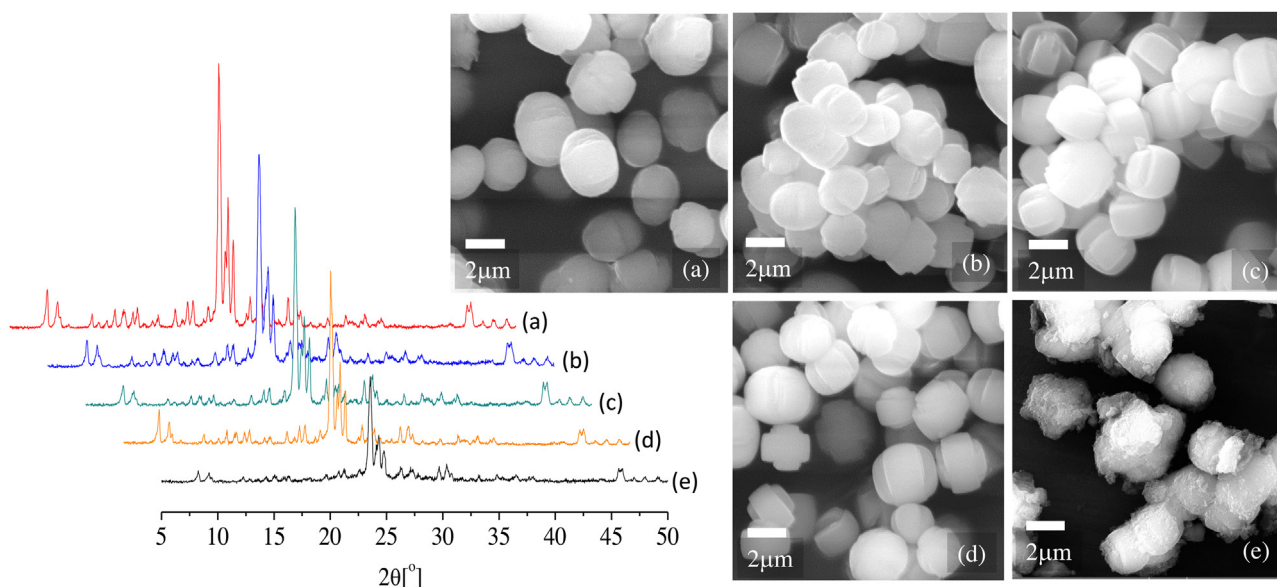


Fig. 1. (A) XRD patterns of as-synthesized borosilicalite-1 (B-MFI, Si/B = 10) zeolite synthesized under microwave irradiation with different mineralizer agent at 180 °C, (B) FE-SEM micrographs of borosilicalite-1 (B-MFI, Si/B = 10) synthesized with different mineralizer agent. (a) KOH/SiO₂ = 0.10, (b) NaOH/SiO₂ = 0.10, (c) NaF/SiO₂ = 0.10, (d) KF/SiO₂ = 0.10, (e) Without alkaline source.

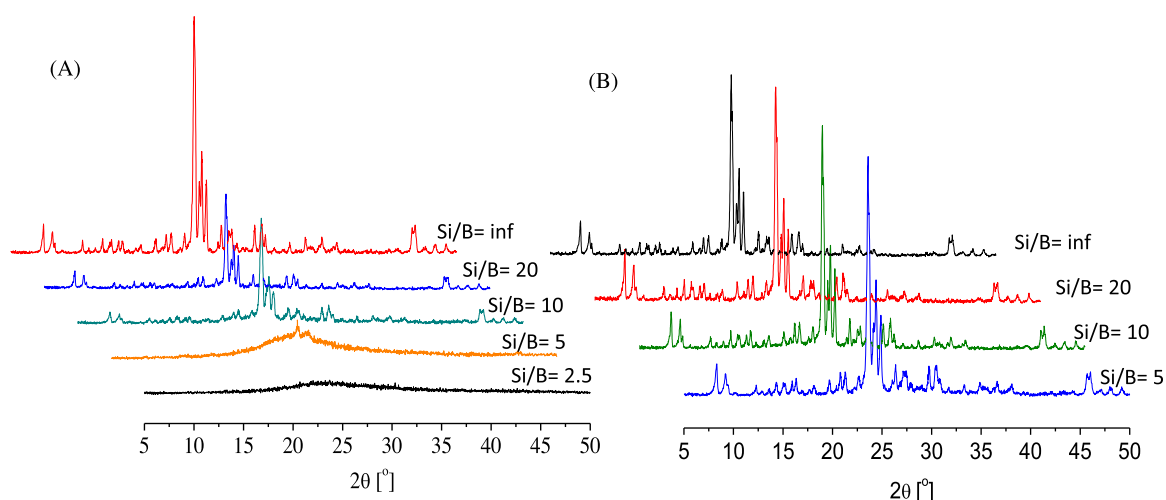


Fig. 2. XRD patterns of borosilicalite-1 (B-MFI) zeolite synthesized under microwave irradiation at 180 °C for 2 h. (A) In the absence of alkaline source, (B) In the presence of sodium hydroxide (NaOH/SiO₂ = 0.10).

3.2. Effect of mineralizer agent source and boron content on textural properties, acidity and zeolitic structure

To determine the effect of mineralizer agent and boron concentration on the textural properties, N₂ sorption were utilized. In the first case, where borosilicalite-1 was synthesized with different mineralizer agents, it was observed that BET isotherm has higher uptake in the presence of sodium hydroxide as shown in Fig. 3A. While the other samples, which were synthesized in the presence of sodium fluoride, potassium fluoride and potassium hydroxide, have almost identical uptake, which indicate that these zeolites exhibit almost identical surface area as shown in Table 2.

On the other hand, when borosilicalite-1 was synthesized in the presence of different contents of boron, as shown in Fig. 3B, the highest uptake was observed in the absence of boron (silicalite-1) due to the availability of larger external surface area. However, the uptake was decreased by the addition of boron and the highest content of boron led to the lower uptake. All adsorption isotherm for

the modified borosilicalite-1 was observed to be in type I isotherm and hysteresis loop was presented, which suggests the association with pore condensation into mesoporous [24].

Nevertheless, it is important to observe the influence of mineralizer agents and boron concentration on the acidity strength and acidity distribution on the zeolite by the ammonium cation exchange. In order to evaluate these effects, temperature-programmed desorption of ammonia (NH₃-TPD) has been utilized. Normally, one or two distinct peaks can be obtained in the zeolitic materials in two temperature regions; low temperature (weak acid) and high temperature (strong acid) region, based on the acidity strength. As shown in Fig. 4, deammoniated borosilicalite-1 has pronounced peak at low temperature region, which implies that boron exhibit in weak acid region due to the nature of boron electronegativity [14]. The expected role of electronegativity on the weakness of the acidity lies in the difficulties of sharing the electron pair from boron to ammonia, which results in weak acid sites.

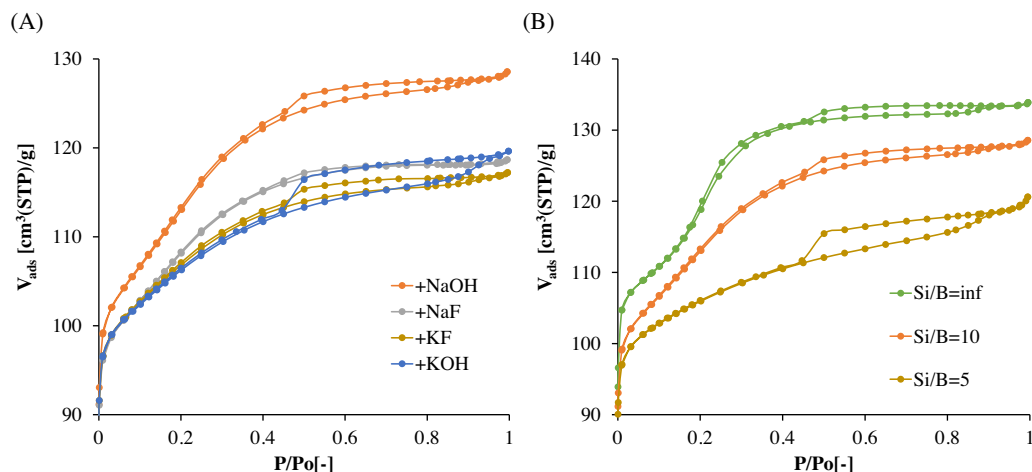


Fig. 3. N_2 adsorption-desorption isotherm of calcined borosilicalite-1 synthesized with (A) different mineralizer agents at Si/B of 10, (B) different Si/B ratios.

Table 2

Textural properties of borosilicalite-1 synthesized with (A) different mineralizer agents, (B) different Si/B ratios.

(A)						
Alkaline source	S_{BET}	S_{micro}^a	S_{ext}^b (t-plot)	V_{total}^c	V_{micro}^d	V_{meso}^e
NaOH	392	249	142	0.199	0.112	0.086
NaF	374	257	117	0.184	0.116	0.068
KF	370	277	93	0.181	0.125	0.057
KOH	368	282	86	0.185	0.127	0.058
(B)						
Si/B ratio	S_{BET}	S_{micro}^a	S_{ext}^b (t-plot)	V_{total}^c	V_{micro}^d	V_{meso}^e
inf	413	225	187	0.207	0.102	0.105
10	392	249	142	0.199	0.112	0.086
5	367	297	69	0.187	0.134	0.053

^at-plot micropore surface area,

^bt-plot external surface area,

^c($p/p_0 = 0.994$),

^dt-plot micropore volume,

^e $V_{meso} = V_{total} - V_{micro}$.

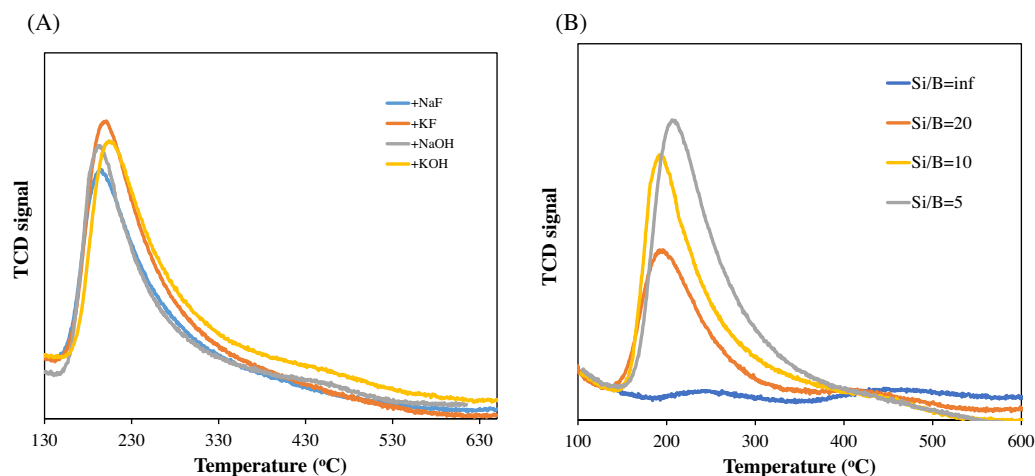


Fig. 4. NH_3 -TPD profiles for calcined borosilicalite-1 zeolite. (A) synthesized with different mineralizer agents at Si/B of 10, (B) synthesized with different Si/B ratios.

The impact of mineralizer agent and boron contents on the acidity of the synthesized zeolites were investigated. It was observed that the degree of boron incorporation in the zeolitic framework of MFI structures are highly affected by the changes in the synthesis parameters. As shown in Fig. 4A, the mineralizer agent has negligible effect on the acidity strength distribution. However, the

negligible change in acidity for different mineralizer agents rely on the ability of the mineralizer agent in enhancing the degree of boron substitution in MFI zeolite framework. Nevertheless, it was reported that content of boron in MFI zeolite is highly affected by the synthesis condition such as the nature of alkaline source and the amount of organic structure directing agent [23]. As shown in

Fig. 4B, the weak acid sites were proportional to the content of boron in the borosilicalite-1, which suggests the increase of the weak acid sites by the increase of boron content on the framework. Whilst the addition of different concentrations of boron led to a conspicuous broadening of the weak acid sites and they were observed to be proportional to the concentration of boron.

NH₃-TPD generally can be used to distinguish the strength of acid sites. The strong acid site in zeolitic materials which was evaluated by NH₃-TPD is mostly a combination of both strong Lewis and/or strong Brønsted acid sites [25,26]. While the weak acid site is attributed to weak Lewis and/or weak Brønsted acid sites [26]. However, in order to distinguish between Lewis and Brønsted acid sites, pyr-FTIR should be employed.

Before we comprehend the Lewis and Brønsted acid sites in borosilicate-1, it is preferred to monitor the FTIR spectra without pyridine adsorption. Infrared spectrum can be used to figure out the fingerprint of the major structural groups of materials such as zeolites. In this study, FTIR spectra was studied towards understanding the nature of the vibrations. The vibrations in zeolitic materials can be caused by either bending or stretching the molecules. Furthermore, the vibration can be internal vibrations of the framework or the vibrations of the external linkage between tetrahedra units. However, the vibrations that related to the external linkages are highly sensitive to the framework structure [27]. As shown in Fig. 5, the peak at the band 450 cm⁻¹ is attributed to Si–O bend in the internal tetrahedra. However, the band at 550 cm⁻¹ are attributed to the double ring vibrations in the external linkage. While the band at 804 cm⁻¹ is attributed to the symmetric stretching vibration of T–O–T in the external linkage. However, the sharp peak at 1053 and 1102 cm⁻¹ are attributed to asymmetric stretching vibrations of T–O–T of zeolite framework (T represent Si or B) and it is sensitive to the content of silicon and boron in the framework. As shown in Fig. 5, it was observed that all samples which were synthesized with different mineralizer agent (Fig. 5A) and samples which were synthesized in the presence of different boron concentrations, have similar vibrational mode.

Quantitative information about acid distribution can be obtained by FTIR detection of pyridine vibration. Two kinds of acids in the frequency range of 1400–1800 cm⁻¹ can be observed by using pyridine as a probe molecule; Brønsted and Lewis acid sites. In typical zeolite samples, three prominent peaks can be observed at 1455, 1490 and 1545 cm⁻¹. However, the most important peaks are shown at the band 1455 and 1545 cm⁻¹, which correspond to the linkage of pyridine to Lewis acid sites (coordinatively bonded) and the adsorption of pyridinium ion on Brønsted acid sites (protonated pyridine), respectively [28]. While the third peak, which is shown at 1490 cm⁻¹, is assigned to a combined contribution from pyridinium ion coordinated to Lewis acid site and adsorbed on Brønsted acid site [29].

Based on these findings, it is worthy to study the pyridine adsorption on borosilicalite-1 to investigate the acidity nature. In the first case, where borosilicalite-1 was synthesized with different mineralizer agents, it was observed that all samples are characterized with Brønsted acid sites as shown in Fig. 6A, while the Lewis acid sites was only observed at 150 °C. However, Lewis acid sites were not observed at 200 °C and 250, which suggest that Lewis acid sites exhibit in weak Lewis form. This observation was also obtained when borosilicalite-1 was synthesized with different boron concentrations (different Si/B ratios) as shown in Fig. 6B, suggesting that boron is exhibit in mainly Brønsted zeolitic form.

The calculated concentrations of the Brønsted acid sites are presented in Table 3. It was observed that the maximum Brønsted acid sites were observed in the presence of sodium as counter ions. Furthermore, it was observed that when the ionic part was F⁻, the acidity was enhanced as compared to OH⁻. Furthermore, the amount of Brønsted acid sites are proportional to the content of

Table 3

Concentration of Brønsted acid sites of borosilicalite-1 synthesized with different mineralizer agents and different Si/B ratios.

Sample	Acid amount (mmol/g)BAS
+NaF	0.0346
+NaOH	0.0276
+KF	0.0250
+KOH	0.0170
Si/B = inf	0.0104
Si/B = 40	0.0170
Si/B = 20	0.0239
Si/B = 10	0.0276
Si/B = 5	0.0281

boron in the borosilicalite-1 which is compatible with the results of NH₃-TPD.

The nature of zeolite surfaces need to be studied due to their importance in the catalytic reactivity. In our studied, infrared spectroscopy was employed to identify the surface silanol groups. As shown in Fig. 7A, silcalite-1 as well as borosilicalite-1 samples, which were synthesized in the presence of different mineralizer agents and different boron contents have an intense peak at 3720 cm⁻¹ attributed to acidic silanol groups [30]. However, it was less intense in case of sodium fluoride due to the enhancement of Si-F rather than Si-O. Silcalite-1 was exhibited in high intense band around 3550 cm⁻¹ which correspond to the presence of silanol nest as shown in Fig. 7B

Solid-state NMR spectra was used to reveal the effect of boron incorporation on the zeolitic structure. Boron containing zeolites such as borosilicalite-1 has been widely characterized by ¹¹B to understand the incorporation type of boron atoms in zeolitic framework. In the first case, where borosilicalite-1 was synthesized in the presence of different mineralizer agents, borosilicalite-1 which was synthesized in the presence of alkali fluoride showed an intense resonance around -3.2 ppm. Furthermore, the resonance band was more intense when the alkali was sodium rather than potassium. This resonance has been ascribed to boron framework in a tetrahedral coordination (B(OSi)₄ site) [16,31,32]. Another resonance was also observed in the resonance range of 0–10 ppm assigned to trigonal coordination system B(OSi)₃. While, on the other hand, when borosilicalite-1 was synthesized in the presence of alkali hydroxide, only resonance assigned to B(OSi)₃ was observed as shown in Fig. 8A. On the other hand, when borosilicalite-1 was synthesized in the presence of sodium hydroxide with different Si/B ratios, trigonal content increased as the increase of boron content as shown in Fig. 8B.

3.3. Effect of mineralizer agent source and boron content on steam catalytic cracking of dodecane

Steam catalytic cracking of dodecane was performed over modified borosilicalite-1 zeolite in a fixed bed reactor at 350 °C. A mixture of 90% n-dodecane and 10% water were fed to the reactor with LHSV of 4 h⁻¹ and the flow rate of nitrogen was kept at 30 mL/min. Fig. 9 shows the catalytic conversion as a function of time-on-stream (TOS). In the first case, where borosilicalite-1 was synthesized with different mineralizer agents, it was observed that borosilicalite-1 samples were almost inactive when borosilicalite-1 zeolites were synthesized in the presence of alkali fluoride as mineralizer agent and it deactivated rapidly. Using fluoride route, the conversion after the first one hour was 30% when the alkali fluoride was potassium fluoride. While, the conversion was much lower when sodium fluoride was used in the synthesis mixture. On the other hand, when borosilicalite-1 zeolite was synthesized in the presence of alkali hydroxide, the catalytic activity was higher and more stable than those which were synthesized in the

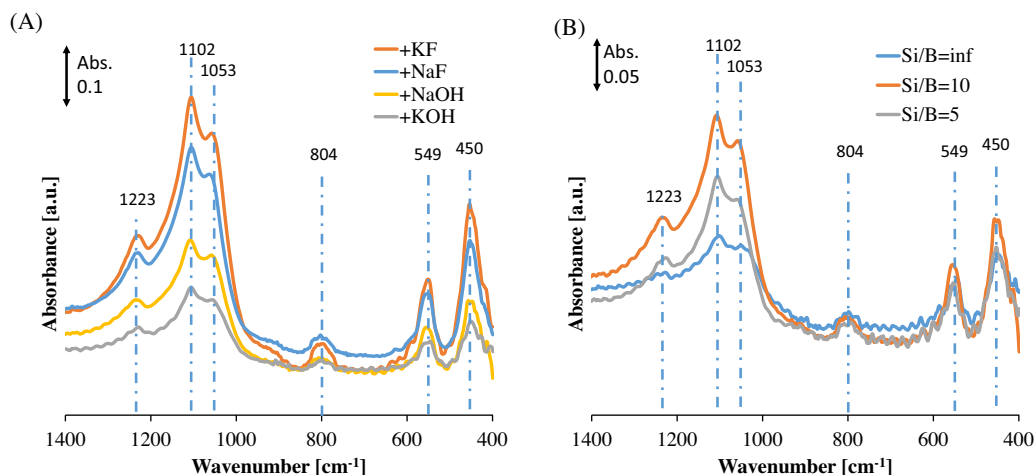


Fig. 5. FTIR profiles of calcined borosilicite-1, (A) synthesized with different mineralizer agents at Si/B of 10, (B) synthesized with different Si/B ratios in the presence of sodium hydroxide.

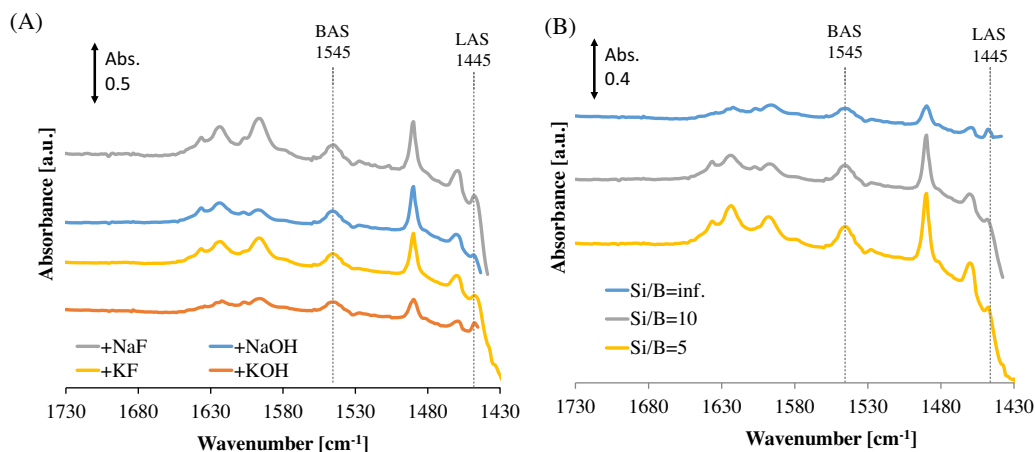


Fig. 6. Pyr-FTIR profiles of borosilicite-1 zeolite. (A) synthesized with different mineralizer agents at Si/B of 10, (B) synthesized with different Si/B ratios.

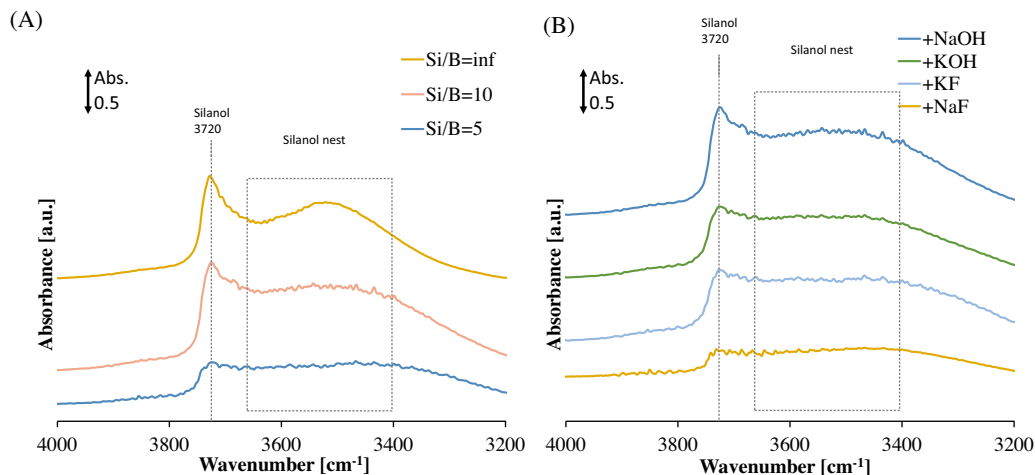


Fig. 7. IR spectra of OH bonds in borosilicite-1 zeolite. (A) synthesized with different mineralizer agents at Si/B of 10, (B) synthesized with different Si/B ratios.

presence of alkali fluoride. When we conduct deeper investigation to explore the influential parameters, we found that sodium hydroxide enhanced the catalytic stability and activity, while those samples which were prepared in the presence of potassium hydrox-

ide were lower in catalytic conversion and catalytic stability as shown in Fig. 9A.

By understanding the physical properties of these samples, we could estimate the influential factors on the catalytic activity and stability. The nature of acidity and its distribution as well as the

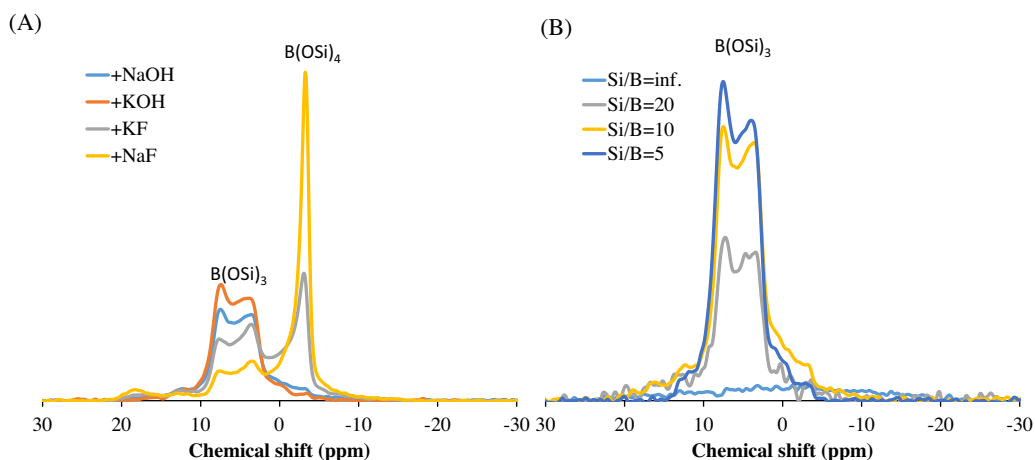


Fig. 8. Solid-state ^{11}B MAS NMR spectra of borosilicalite-1 zeolite. (A) synthesized with different mineralizer agents at Si/B of 10, (B) synthesized with different Si/B ratios.

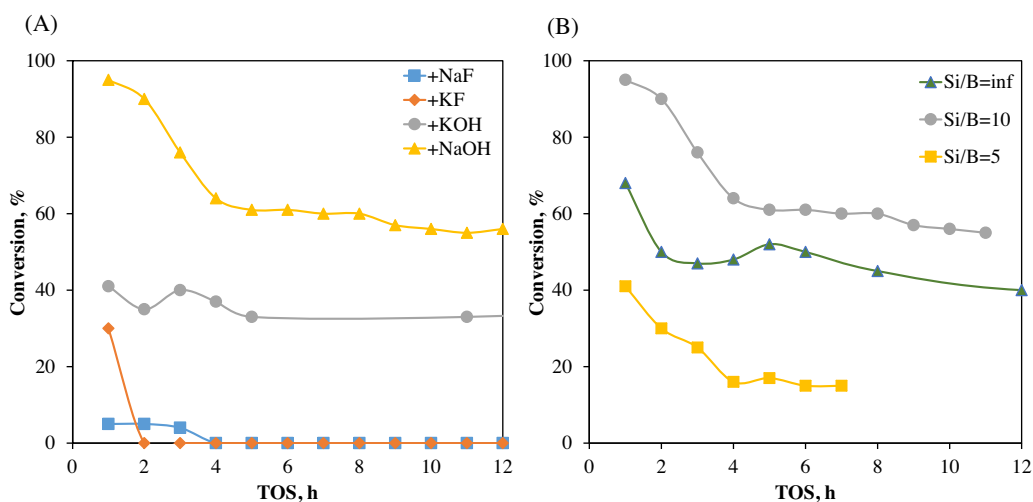


Fig. 9. Steam catalytic conversion of C12 at 350 °C, 10% water, 90% dodecane. (A) synthesized with different mineralizer agents at Si/B of 10, (B) the effect of Si/B ratio in the presence of sodium hydroxide as mineralizer agent. (A) Si/B = 10 (before reaction) (B) Si/B = 10 (after reaction).

zeolitic structure can be correlated to end up with the steering parameter that led to the variation on catalytic activity. From XRD analysis, we found that all samples of borosilicalite-1 which were synthesized in the presence of different mineralizer agents were confirmed to have MFI structure and almost identical in crystallinity. Furthermore, it was observed that borosilicalite-1 can be obtained with higher crystallinity when samples were synthesized in the presence of alkali hydroxides as shown in Fig. 1. While those samples which were synthesized in the presence of alkali fluorides, found to be relatively lower in crystallinity. However, this reduction in crystallinity was limited and can be assumed to be negligible. From SEM as shown in Fig. 1, we observed that these samples are all exhibit in almost identical particle size and morphology and we can assume that the effect of these two parameters (particle size and morphology) in catalytic activity are negligible. From BET isotherm which is shown in Fig. 3, we can observe clearly that samples which were synthesized in the presence of sodium hydroxide has higher uptake, which suggest that borosilicalite-1 synthesized in the presence of sodium hydroxide has the ability to absorb larger quantity in their micropores and mesopore as compared to the samples which were synthesized in the presence of other mineralizer agents. As a result, larger absorption-desorption process lead to faster catalytic achievement as far as the active site are available. Additional outcome observed from BET analysis, that borosilicalite-1 which were

synthesized in the presence of sodium hydroxide found to be exist with higher external surface area and this confirmed through the course of the study as compared to the other samples. Exclusively, we could say that textural properties are very important for the successful catalytic reaction in dodecane cracking over borosilicalite-1. Catalytic acidity were observed to be in weak acid site as shown from NH_3 -TPD in Fig. 4 and was observed to be identical in all borosilicalite-1 samples which were synthesized in the presence of different mineralizer agents. Further confirmation of the acidity nature were proved by the pyr-FTIR and it was observed to be varied in a small range in brønsted acid site. Although it found that this variation is small, we could say that the contribution of these minor changes in acidity is not the primary factor in the catalytic activity over borosilicalite-1 as compared to external surface area and the limit of the uptake so far. When the structural properties were discovered as shown in Fig. 8, it found that alkali hydroxide or fluorides affected the coordination of borosilicalite-1 accordingly. Once alkali hydroxide were used, trigonal coordination were obtained. On the other hand, when alkali fluoride were used in the synthesis of borosilicalite-1, a combination of trigonal and tetragonal coordination systems were obtained. Where the trigonal was enhanced by the presence of tetrapropyl ammonium hydroxide which was used as organic structure directing agent. The availability of OH functionality was limited and hence the availability of trigonal was also

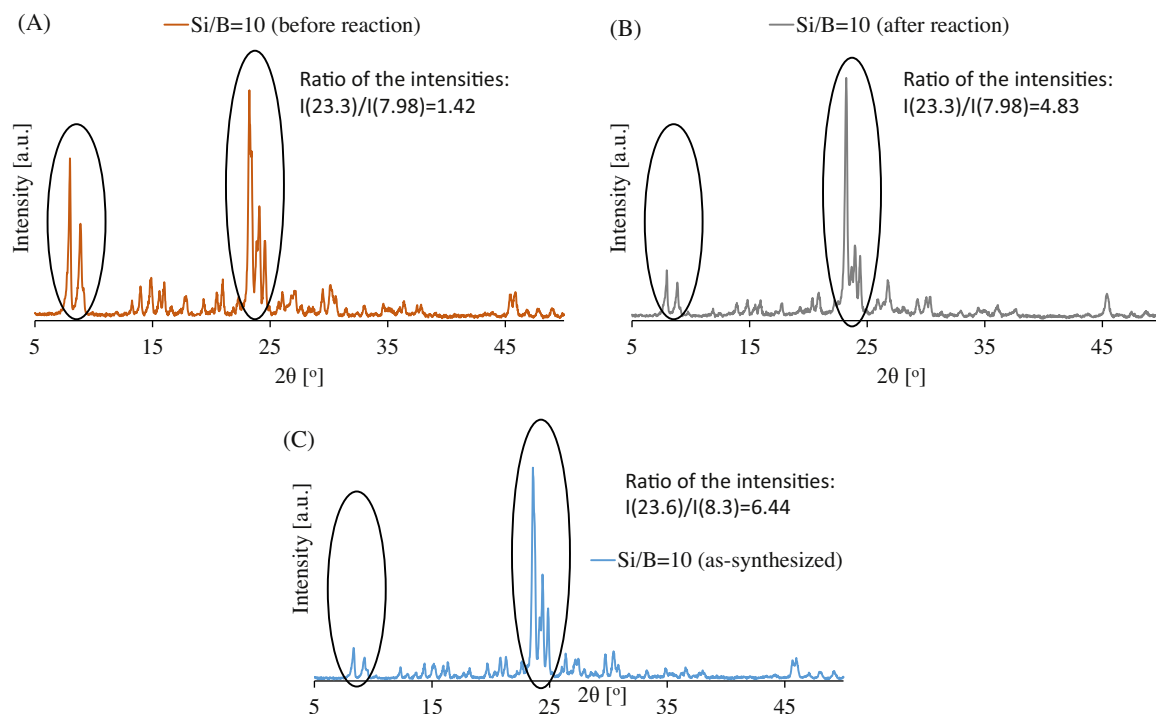


Fig. 10. XRD patterns of H-borosilicalite-1, (A) H-borosilicalite-1 before reaction and (B) after 12 h of reaction in stream, (C) as-synthesized borosilicalite-1 zeolite.

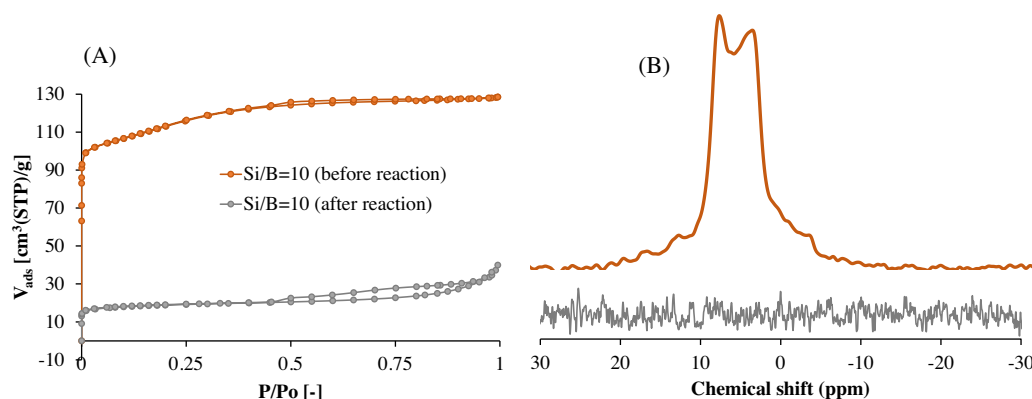


Fig. 11. (A) BET isotherm, (B) Solid-state ^{11}B MAS NMR spectra of borosilicalite-1 synthesized with Si/B ratio of 10 in the presence of sodium hydroxide as a mineralizer agent.

limited in both samples which were prepared by sodium hydroxide and potassium hydroxide. Although some of trigonal coordination were observed in those samples which were prepared using alkali fluoride, the effect of extremely high electronegativity of fluoride ions were mostly the dominant in the catalytic activity by limiting the chairing of electrons, the contribution of Brønsted acid sites or Lewis acid site through the course of reaction. This why the catalytic reaction was limited. Furthermore, it was observed that sodium fluoride has more intense resonance for the tetrahedral coordination as compared to borosilicalite-1 which was synthesized in the presence of potassium hydroxide. This order is absolutely exactly comparable to the order of catalytic conversion. Maximum trigonal coordination and minimum tetrahedral coordination lead to higher catalytic conversion for same acidic condition, silanol condition and textural properties. But question comes to mind, why borosilicalite-1 in the presence of potassium hydroxide has lower catalytic activity than the samples synthesized in the presence of sodium hydroxide even though it has larger trigonal coordination. The reason is that borosilicalite-1 which were synthesized in the

presence of potassium hydroxide has smaller acidity, silanol and silanol nest and smaller external surface area. We could conclude that higher steam catalytic activity and catalytic conversion can be obtained as far we have larger external surface area, larger silanol and silanol nest, larger acid strength and optimum trigonal content with no tetrahedral coordination, which means that these factor playing a curtail role in the steam catalytic cracking of n-dodecane.

Further investigation over the best sample, which showed perfect textural properties, trigonal coordination system and higher catalytic activity to visualize the reasons for deactivation through the reaction time. This investigation were carried out over borosilicalite-1 which were synthesized with Si/B ratio of 10 in the presence of sodium hydroxide as mineralizer agent. From XRD results on Fig. 10, we observed a variation on the XRD patterns between the pattern of the as-synthesized borosilicalite-1, and the sample before and after catalytic reaction. In MFI zeolites, we observed that the intensities of the patterns which appear in the range of 2θ between 5 and 20 and with that at 2θ of 23 were comparably related. When the sample was in the as-synthesized form,

Table 4

Textural properties of borosilicalite-1 synthesized with Si/B ratio of 10 in the presence of sodium hydroxide as mineralizer agent before and after reaction.

	Si/B ratio	S_{BET}	S_{micro}^a	S_{ext}^b (t-plot)	V_{total}^c	V_{micro}^d	V_{meso}^e
(Before reaction)	10	392	249	142	0.199	0.112	0.086
(After reaction)	10	61	40	20	0.062	0.020	0.042

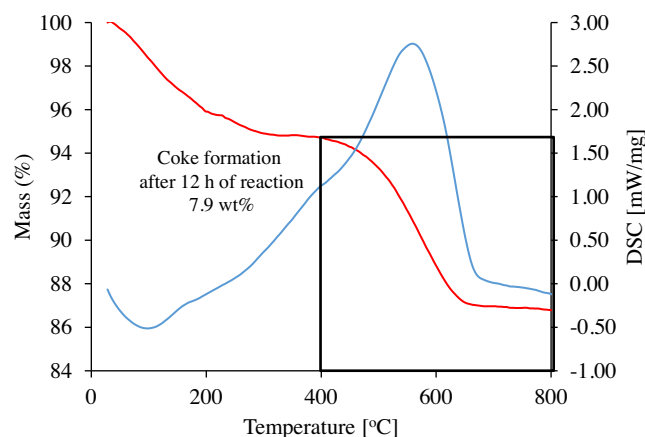
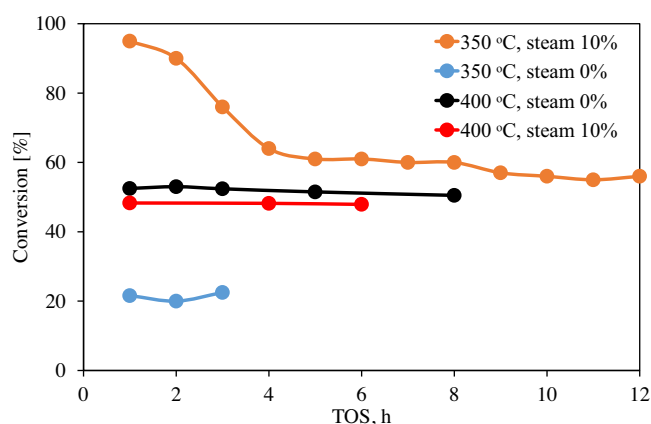
^at-plot micropore surface area,^bt-plot external surface area,^c(p/p0 = 0.994),^dt-plot micropore volume,^e $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.**Table 5**

Conversion and product distribution over borosilicalite-1 synthesized with sodium hydroxide and sodium fluoride as mineralizer agent.

	Time, h	Conversion%	Naphthenes C6,C7 %	Paraffins%	Aromatics%	Olefins C5=C6=C7 %
NaF	1	3	0.00	56.88	0.00	43.10
NaOH	1	95	6.98	47.56	35.25	10.21

the ratio of the intensity at 2 θ of 23 to the intensity at 2 θ of 8 was the maximum. Once the sample was calcined and it was in proton form (H-Borosilicalite-1), the intensity ratio was the minimum. However, used catalyst showed a results in between. To investigate further, samples before calcination has the organic structure with other elements, which mainly consists of carbon and hydrogen as the content of the template, sodium and so on. Once the sample calcined and ion exchanged properly, the internal cages and channels became empty and its cages and channels were ready for the catalytic reactions. However, through the course of reaction, deactivation happened and coke was formed. As a results, channels and cages were filled again with the coked materials, which was mainly carbons. And hence again, the XRD patterns show similar trend as it was observed in the as-synthesized pattern. And it is expected that the ratio can be similar after further filling with carbons to reach to the maximum point of the filling and lead to almost similar ratio. To confirm that finding, BET analysis was applied for the sample after the catalytic cracking of dodecane as shown in Fig. 11(A) and Table 4. During this investigation, it was found that the uptake of the zeolite was reduced in order of magnitude and the monolayer filling limit was reduced from 82.06 to 13.96 cm³/g STP. Furthermore, BET surface area and external surface area reduced from 392 and 142 m²/g to 61 and 20 m²/g, respectively, which supported that the reason for deactivation was the reduction in the textural properties. Solid-state ¹¹B MAS NMR spectra of the samples were investigated to observe the effect of steam in boron and borosilicalite-1 structure as shown in Fig. 11(B). It was found that borosilicalite-1 was affected by the presence of steam, which led to deboronation. As a recommendation for further experimental plan, novel methods need to be investigated in order to prevent the deboronation through steam catalytic cracking by adding materials such as phosphoric acid through post-treatment, which could stabilizes the catalytic materials as well as preserving the boron. For this sample, coke was estimated as shown in Fig. 12 and found to be 7.9% after 12 h of reaction.

Catalytic activity over borosilicalite-1 at Si/B ratio of 10 synthesized in the presence of sodium hydroxide as mineralizer agent was investigated with and without steam at different temperatures as shown in Fig. 13. It was observed that steam played a critical role in catalytic cracking of dodecane. When the steam was absent, the catalytic conversion was only 20% and it was stable over that tested period (4 h) at 350 °C. However, when the temperature of the catalytic cracking was increased from 350 to 400 °C, the catalytic conversion in the absence of steam was increased and reached to 52.5% and it was stable over the tested range (8 h). On the other hand, when the catalytic activity was evaluated at higher temperature (400 °C) in the presence of steam, the deboronation was observed in less than 1 h due to the high temperature of steam

**Fig. 12.** Coke formation studied by TGA for borosilicalite-1 synthesized with Si/B ratio of 10 in the presence of sodium hydroxide as mineralizer agent before and after reaction.**Fig. 13.** Steam catalytic conversion over H-borosilicalite-1 synthesized with Si/B ratio of 10 in the presence of sodium hydroxide as mineralizer agent with different catalytic conditions.

and led to the catalytic conversion of 48% and was stable over the tested period (6 h). As a recommended point, a novel method will be applied in future to stabilize the boron by post-treatment and to be applicable for the catalytic cracking with steam at higher temperature.

The optimum trigonal coordination has led to activating or deactivating the catalytic performance on dodecane cracking. When MFI zeolite were synthesized in the presence of different boron

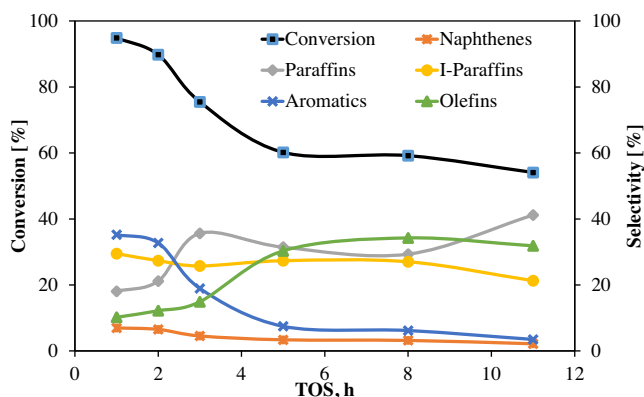


Fig. 14. PIONA results for steam catalytic conversion and selectivity of C12 at 350 °C, 10% water, 90% dodecane for borosilicalite-1 synthesized in the presence of sodium hydroxide with Si/B of 10.

concentrations, silicalite-1 has catalytic conversion of 68% for the first one hour. However, it was deactivated gradually until the conversion reached to 40% after 12 h of reaction-on-stream. However, this catalyst is not controlled by the trigonal coordination since boron was absent. But, other parameters such as textural properties and acidity can control the catalytic activity. When boron was absent, the silicalite-1 samples is characterized with larger acidic silanol content and silanol nest as shown in Fig. 7B. This contributed in maintaining the catalytic activity. However, when boron was added to the synthesis mixture, borosilicalite-1 with Si/B ratio of 10, showed extremely higher activity and the catalytic conversion reacted to 95% after the first one hour. Stability, on the other hand, was observed to be the most stable and the catalytic conversion reached to 56% after 12 h. While, on the other hand, going beyond the optimum trigonal coordination content led to lower conversion as shown in borosilicalite-1 which was synthesized with Si/B ratio of 5 as shown in Fig. 9B.

However, when boron was added, the acidic silanol were reduced and the catalytic activity was compensated by the presence of weak acid site contributed from boron. Still the absence of acidic silanol and presence of some tetrahedral boron in the system contributed to the fast deactivation. Nevertheless, further increase in boron content could lead to faster deactivation. Maintaining the acidity, increasing the acidic silanol and silanol nest and maintaining the coordination structure of borosilicalite-1 to trigonal coordination system, all are contributing in increasing the catalytic activity and stability of steam catalytic cracking of n-dodecane.

Catalytic selectivity was estimated for the best samples of borosilicalite-1 which was synthesized in the presence of sodium hydroxide as mineralizer agent and Si/B ratio of 10 using Paraffin, Isoparaffin, Aromatic, Naphthalene, or Olefin (PIONA) GC. As shown in Fig. 14, product was containing paraffin, i-paraffin, naphthalene, olefin and aromatics. Higher selectivity towards olefins, paraffins and i-paraffins were obtained. However, the selectivity towards aromatics were reduced as the catalytic conversion was reduced.

Two reaction stages over micro borosilicalite-1 zeolite was observed; primary cracking and secondary reaction. In primary cracking, the product is mainly olefins, paraffins and hydrogen. While in secondary reaction, further reaction converts the products from primary cracking over shape selectivity pore of ZSM-5 to form aromatics, naphthalene, isomers via H-transfer, transalkylation, cyclization and further dehydrogenation. The primary and secondary reactions over shape selectivity were active for dodecane conversion. For the first two hours, the selectivity of cyclization to aromatics and naphthenes were maintained in the range of 38–40%. But after the third hour, a decline of pore selectivity for cyclization was observed, but the transalkylation of iso-paraffins was

maintained at the same level of selectivity. During the decline of shape selectivity in the secondary reaction, the primary cracking increased and produced higher olefins and alkanes. Nevertheless, the shape selectivity of transalkylation as secondary reaction, which formed iso-paraffins during reaction stream, was maintained constant.

Catalytic activity over different mineralizer agents were studied and the catalytic activity were found to be higher in the presence of alkali hydroxide. However, in term of selectivity, we studied the selectivity profile for samples synthesized with sodium hydroxide and sodium fluoride for the first 1 (one) hour of the reaction as shown in Table 5. It was observed that the difference is mainly in the selectivity towards aromatics and olefins. When sodium hydroxide was used as a mineralizer agent, it found that aromatics formed with high selectivity reached to 35% and the selectivity towards olefin was 10%. On the other hand, when sodium fluoride was used as mineralizer agent, aromatics formation was not observed and the formation of olefins was high up to 43%.

4. Conclusions

Microwave irradiation was utilized to synthesize borosilicalite-1 (B-MFI) with different mineralizer agents to improve steam catalytic cracking of dodecane. The isomorphous substitution of boron in zeolitic framework has a curtail role in adjusting the zeolitic acidity. It was observed that the amount of weak acid sites was proportional to the contents of boron and the acid site distributions were shown to be in Brønsted acid site forms. It was found that borosilicalite-1 was more stable when it was synthesized in the presence of sodium hydroxide as mineralizer agent. In this case, the catalytic conversion was reached to 95% at 350 °C with space velocity of 4 h⁻¹ when the Si/B ratio was 10. It was observed that maintaining the acidity, increasing the acidic silanol and silanol nest and maintaining the coordination structure of borosilicalite-1 to trigonal coordination system, all are contributing in increasing the catalytic activity and stability of steam catalytic cracking of n-dodecane.

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